



Influence of alcoholic and carbonyl functions in microwave-assisted and photo-assisted oxidative mineralization

Satoshi Horikoshi^{a,b,*}, Masahiko Abe^a, Nick Serpone^{c,**}

^a Research Institute for Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda-shi, Chiba-ken 278-8510, Japan

^b Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan

^c Dipartimento di Chimica Organica, Università di Pavia, Via Taramelli 10, Pavia 27100, Italy

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ABSTRACT

The tendency of water-soluble organics to be photomineralized under microwave and UV irradiation was examined using model substrates bearing alcoholic (methanol, ethanol 1-propanol, ethylene glycol and glycerin) and carbonyl functions (acetone, formic acid and acetic acid). Trends were seen from the decrease of the kinetics of loss of total organic carbon (TOC) with irradiation time. Microwave thermal and specific (non-thermal) effects were probed for the photomineralization process on irradiation of TiO₂ suspensions with 2.45-GHz microwaves and UV irradiation with conventional heating under otherwise identical temperatures, and relative to UV irradiation alone to assess the thermal (TH) and microwave (MW) factors. Dielectric properties of each substrate were also determined under the experimental conditions used.

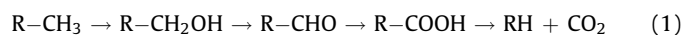
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1. Introduction

Recent years have witnessed reports of studies in which microwaves were shown to enhance the degradation of organic pollutants in the presence of the metal oxide TiO₂ [1–3]. Although microwave radiation has been widely used domestically as a heating source in food cooking [4], it has also been used to improve the catalytic properties of some metal oxides. Of particular interest are the special effects imparted by microwaves as evidenced in various reports in heterogeneous catalysis with metal catalysts applied to organic syntheses [5]. In this regard, we recently reported on microwave specific effects that impact on the Raney-Ni and Urushibara-Ni catalysts having different physical and chemical properties from experiments on conventional and microwave dielectric heating of solutions at otherwise identical temperatures [6]. Specific effects of microwaves are not always observed in heterogeneous catalysis. More precisely, except perhaps for some cases, catalyzed reactions are mostly influenced by the microwave (MW) thermal (TH) effect. Accordingly, it is important to clarify the features and tendencies of the microwave effects as to whether they are simply thermal and/or non-thermal

in nature in catalyzed processes, failing which the microwave radiation will remain a mere heat source. In photoassisted reactions subjected to microwave irradiation conditions, the microwave effect(s) can be ascribed either to the thermal or non-thermal effect, or to both. Some of our recent work has focused on examining such effects from the viewpoint of changes in physical and chemical properties of TiO₂ [7] and from mechanistic studies of the degradation of model toxins exposed to microwave and non-microwave irradiation conditions [8–10].

The current study examines microwave specific effects in relation to the chemical structure of low molecular weight compounds, whose photoassisted mineralization in the presence of titanium dioxide yields formation of CO₂ gas by an oxidation process via alcohol, aldehyde, and carboxylic acid intermediates (reaction (1)) [11]. Delineating the effect of microwave radiation on these compounds may provide an important base for clarifying degradation and mineralization mechanistic features.



2. Experimental

2.1. Materials

Titanium dioxide was Degussa P-25 grade. High-purity grade methanol, ethanol, 1-propanol, ethylene glycol, glycerin, acetone, formic acid and acetic acid, used as the model substrates, were

* Corresponding author at: Research Institute for Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda-shi, Chiba-ken 278-8510, Japan.

** co-Corresponding author.

E-mail addresses: horikosi@rs.noda.tus.ac.jp (S. Horikoshi), nickser@alcor.concordia.ca, nick.serpone@unipv.it (N. Serpone).

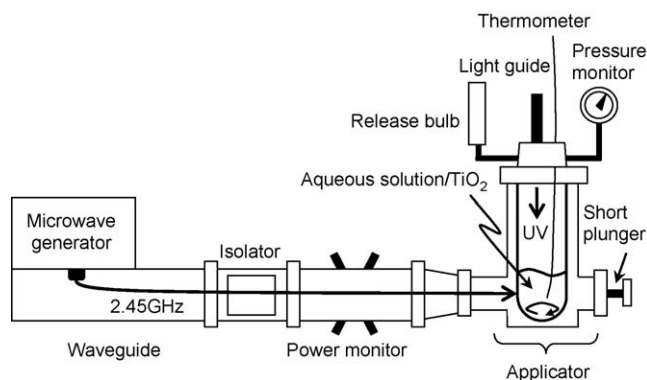


Fig. 1. Experimental setup used in the photoassisted mineralization of alcoholic and carbonyl substrates in aqueous TiO_2 powdered dispersions using a UV light source and a source of microwave radiation.

obtained from Tokyo Kasei Kogyo Co. Ltd. Temporal changes in the loss of total organic carbon (TOC) during the degradation of these substrates were monitored with a Shimadzu TOC-5000A analyzer.

2.2. Experimental reactor setup

Continuous microwave irradiation was achieved using a 2.45 GHz microwave generator (maximal power, 800 W), a power monitor, and an isolator (air cooling device) fabricated by Hitachi Kyowa Engineering Co. Ltd. (Fig. 1). The 30-W continuous microwaves emitted from the magnetron of the microwave source were measured using the power monitor.

To the extent that dielectric factors might play a role in the degradation of substrates, we determined experimentally the dielectric loss factors (ϵ'') and the dielectric constants (ϵ') using an Agilent Technologies HP-85070B Network Analyzer. The dielectric loss tangent ($\tan \delta = \epsilon''/\epsilon'$) and the microwave penetration depths (cm) were calculated using a method reported earlier [7,12]. Note that the dielectric loss factor reflects the degree to which the electromagnetic energy of the microwaves is transformed into thermal energy (heat) – the so-called dielectric heating. The relevant data are reported in Table 1.

2.3. Procedures

An aqueous solution of a substrate (30 mL; 0.50 mM) containing the P-25 TiO_2 powder (loading, 60 mg; 2 g L^{-1}) was introduced into a closed high-pressure 150-mL Pyrex glass cylindrical reactor (Taiatsu Techno Co.; size, 160 mm (H) \times 37 mm (i.d.); maximal pressure, 1 MPa) from the top side and subsequently irradiated with a Toshiba 75-W high-pressure mercury lamp (irradiance ca. 0.40 mW cm^{-2}) through a fiber optic. The solution temperature was measured with a K-type thermocouple. The reactor was sealed

with two Byton O-rings and a stainless steel cap. A pressure gauge and a release bulb were connected to the cover of the reactor. The cylindrical reactor was sealed with a silicone O-ring and covered with a stainless steel cap in the batch mode. The reaction mixture was continually stirred magnetically. We confirmed that the magnet bar used to stir the suspension was not a secondary heat source under microwave irradiation.

Different protocols were examined to achieve the mineralization of the model substrates: (i) photoassisted degradation of air-equilibrated TiO_2 dispersions by UV irradiation alone (TiO_2/UV protocol), (ii) photoassisted degradations of the substrates in air-equilibrated TiO_2 dispersions under UV light and microwave irradiation ($\text{TiO}_2/\text{UV}/\text{MW}$ protocol) and (iii) thermally assisted photodegradation of the dispersions with UV light and externally applied conventional heat ($\text{TiO}_2/\text{UV}/\text{CH}$ protocol) supplied by coating one part of the cylindrical photoreactor with a thin metallic film on one side and at the bottom of the reactor. The uncoated side was used to allow for UV irradiation of the reactor contents. The rate of increase of temperature (error $\leq \pm 1^\circ \text{C}$) and the pressure generated in the $\text{TiO}_2/\text{UV}/\text{CH}$ protocol were maintained at levels otherwise identical to those generated for the $\text{TiO}_2/\text{UV}/\text{MW}$ method.

3. Results and discussion

The temporal losses of total organic carbon on irradiation of the various dispersions by the TiO_2/UV , $\text{TiO}_2/\text{UV}/\text{CH}$ and $\text{TiO}_2/\text{UV}/\text{MW}$ methods are illustrated in Fig. 2a–h, respectively. Quantitative rate data are reported in Table 2.

3.1. Mineralization of substrates with an alcoholic function

3.1.1. Methanol

The rate of mineralization of methanol by the $\text{TiO}_2/\text{UV}/\text{MW}$ method was nearly threefold faster than by the $\text{TiO}_2/\text{UV}/\text{CH}$ protocol, even though the temperatures at which the process occurred were identical. This difference in the kinetics obtained under otherwise identical conditions can only be ascribed to a microwave specific effect (the MW factor – Table 2). As well, the thermal effect is also not insignificant – the photoassisted mineralization of this substrate under conventional heating is nearly an order of magnitude faster; e.g. compare the $\text{TiO}_2/\text{UV}/\text{CH}$ method with the TiO_2/UV protocol (the TH factor).

3.1.2. Ethanol

Adding one C atom to methanol caused no changes in the kinetics of the photoassisted mineralization of this substrate by the TiO_2/UV protocol. By contrast, the rates were significantly attenuated for the $\text{TiO}_2/\text{UV}/\text{CH}$ and $\text{TiO}_2/\text{UV}/\text{MW}$ by factors of ~ 3 and 3.8, respectively. The thermal factor also caused a threefold increase in the rate of mineralization, whereas the MW effect was somewhat subdued (1.3; see last column of Table 2) indicating that the MW effect was somewhat limited relative to the TH factor.

3.1.3. 1-Propanol

With the addition of two C atoms to methanol, both the TH and the MW factors no longer seemed to play a role in the mineralization of this substrate. The kinetics of mineralization were practically identical.

3.1.4. Ethylene glycol

Relative to methanol, this substrate contains an additional C atom as well as an additional OH function. The data in Table 2 demonstrate that the TH effect is considerably attenuated; i.e. the rate of mineralization by the $\text{TiO}_2/\text{UV}/\text{CH}$ method relative to the

Table 1
Dielectric loss factors (ϵ''), dielectric constants (ϵ'), dielectric loss tangent ($\tan \delta$) and microwave penetration depths (cm) for methanol, ethanol, 1-propanol, ethylene glycol, glycerin, acetone, formic acid and acetic acid (temperature, 24–26 $^\circ \text{C}$).

	Dielectric loss factor (ϵ'')	Dielectric constant (ϵ')	Dielectric loss tangent ($\tan \delta$)	Penetration depth (cm)
Water	8.52	75.9	0.11	1.99
Methanol	21.5	32.6	0.66	0.52
Ethanol	22.8	24.3	0.94	0.42
1-Propanol	15.2	18.3	0.76	0.55
Ethylene glycol	50.0	37.0	1.35	0.24
Glycerin	28.0	43.0	0.65	0.45
Acetone	1.12	20.7	0.054	7.89
Formic acid	42.2	58.5	0.72	0.35
Acetic acid	1.08	6.2	0.17	4.48

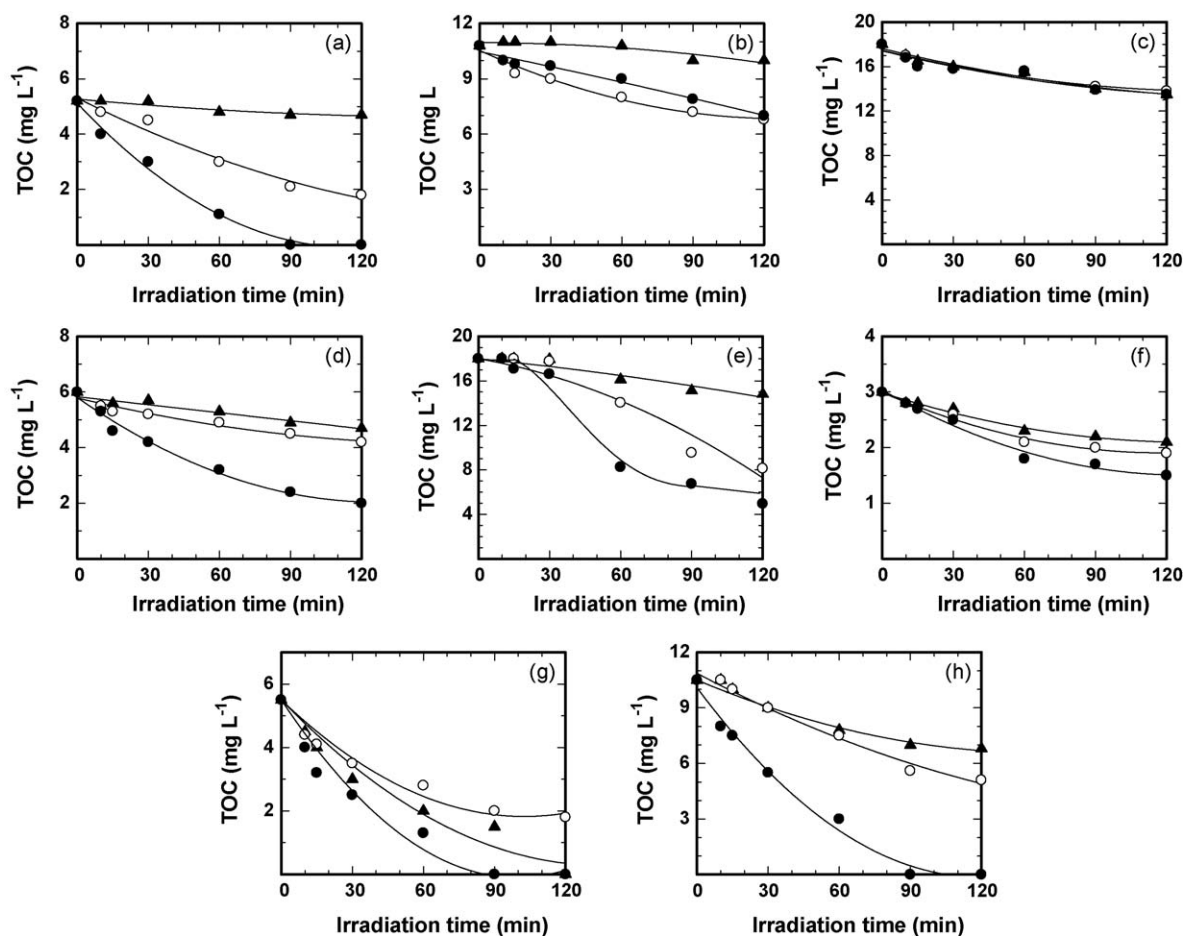


Fig. 2. Temporal loss of total organic carbon in the mineralization of aqueous solutions of the model substrates: (a) methanol, (b) ethanol, (c) 1-propanol, (d) ethylene glycol, (e) glycerin, (f) acetone, (g) formic acid and (h) acetic acid by the photooxidation process. (\blacktriangle) TiO_2/UV ; thermally/photo-assisted oxidation (\circ) $\text{TiO}_2/\text{UV}/\text{CH}$; and by an integrated microwave-/photoassisted degradation protocol, (\bullet) $\text{TiO}_2/\text{UV}/\text{MW}$.

photoassisted TiO_2/UV protocol is just slightly faster. By contrast, the MW factor caused a significant fourfold increase in the rate of mineralization of ethylene glycol, whereas the combined TH–MW effect led to a nearly sixfold increase in the kinetics.

Table 2

Kinetics (k) in the loss of TOC for 0–120 min of irradiation by the TiO_2/UV , $\text{TiO}_2/\text{UV}/\text{CH}$ and $\text{TiO}_2/\text{UV}/\text{MW}$ methods, except for methanol, formic acid and acetic acid that were irradiated only for 0–90 min. TH factor: increased rate by $\text{TiO}_2/\text{UV}/\text{CH}$ protocol relative to TiO_2/UV ; TH–MW factor: increased rate by $\text{TiO}_2/\text{UV}/\text{MW}$ method relative to TiO_2/UV ; and MW factor: increase in rate by the $\text{TiO}_2/\text{UV}/\text{MW}$ protocol with respect to $\text{TiO}_2/\text{UV}/\text{CH}$.

	Mineralization rate constants, $k_{\text{TOC}} (\times 10^{-3} \text{ min}^{-1})$			Increase in rates by different factors		
	TiO_2/UV	$\text{TiO}_2/\text{UV}/\text{CH}$	$\text{TiO}_2/\text{UV}/\text{MW}$	TH ^a	TH–MW ^b	MW ^c
Methanol	1.0	9.1	25.3	9.1	25.3	2.8
Ethanol	0.9	2.7	3.4	3.0	3.8	1.3
1-Propanol	2.0	1.8	2.1	0.9	1.0	1.2
Ethylene glycol	1.6	2.2	9.0	1.4	5.6	4.1
Glycerin	1.8	6.3	11.9	3.5	6.6	1.9
Acetone	2.7	3.6	6.0	1.3	2.2	1.7
Formic acid	8.4	11.3	23.1	1.3	2.7	2.0
Acetic acid	3.9	6.1	20.5	1.6	5.3	3.4

^a Thermal factor by comparing the k_{TOC} between the $\text{TiO}_2/\text{UV}/\text{CH}$ relative to TiO_2/UV .

^b Thermal factor caused by the microwave irradiation on comparing the k_{TOC} obtained from the $\text{TiO}_2/\text{UV}/\text{MW}$ method relative to TiO_2/UV .

^c Microwave factor from the comparison of k_{TOC} 's from the $\text{TiO}_2/\text{UV}/\text{MW}$ method relative to the $\text{TiO}_2/\text{UV}/\text{CH}$ protocol.

3.1.5. Glycerin

The structure of glycerin contains three C atoms and three OH functions, i.e. one additional $-\text{CH}_2-\text{OH}$ unit with respect to ethylene glycol. The dynamics of the photoassisted mineralization of these two highly OH-loaded substrates by the TiO_2/UV protocol are experimentally similar. However, the TH factor increased the rates substantially by nearly a factor of 3.5 as evidenced by comparing the TiO_2/UV method with the $\text{TiO}_2/\text{UV}/\text{CH}$ protocol. The MW factor also impacted on the mineralization of this substrate with the rate of mineralization by the $\text{TiO}_2/\text{UV}/\text{MW}$ method being twofold faster than by the $\text{TiO}_2/\text{UV}/\text{CH}$ protocol. Just as evidenced for ethylene glycol, the mineralization process for glycerin and the corresponding TH and MW factors are somewhat attenuated relative to methanol, yet the photoassisted process (TiO_2/UV protocol) was enhanced, albeit to a small extent relative to methanol. Evidently, both the number of $-\text{CH}_2-$ units and $-\text{OH}$ functions play a role in either promoting or attenuating the degradation of the substrates with the assistance of the TH and MW effects.

3.2. Substrates with CO functions

3.2.1. Acetone

The TH effect and the MW effect had only a small influence on the dynamics of mineralization of acetone, whereas the rate of the photoassisted mineralization by the TiO_2/UV protocol was not very different from that of 1-propanol.

3.2.2. Formic acid

Of all the substrates examined, formic acid was mineralized faster by UV irradiation of the aqueous TiO_2 suspension. Compared to methanol, the dynamics of mineralization for the $\text{TiO}_2/\text{UV}/\text{CH}$ and $\text{TiO}_2/\text{UV}/\text{MW}$ protocols were rather similar. Regardless, while the TH factor is significantly different from that of methanol (1.3 versus 9.1; see column 5 of Table 2), the MW effect is only slightly smaller (2.0 versus 2.8).

3.2.3. Acetic acid

The rates of mineralization of acetic acid were about twofold slower for both the TiO_2/UV and $\text{TiO}_2/\text{UV}/\text{CH}$ methods relative to formic acid, whereas the rates for the $\text{TiO}_2/\text{UV}/\text{MW}$ method were rather similar. However, even though the influence of the TH factors were similar for both formic and acetic acids, the MW effect was somewhat greater for the latter.

It is interesting to note that, except for ethylene glycol and acetic acid, the sum of the TH effect and the MW effect do not correlate with the combined TH–MW effect. The difference is particularly significant for methanol. There is a positive synergistic effect between the TH and MW factors in the mineralization of methanol, ethanol and glycerin. In the case of 1-propanol, acetone and formic acid the synergistic effect is negative. That is, the TH–MW factor is greater (positive) than the sum of the TH and MW factors for methanol, ethanol and glycerin, whereas the TH–MW factor is smaller (negative) than the sum, in the latter cases.

3.3. Effect(s) of the number of C atoms and OH functions on mineralization

3.3.1. Number of carbons

For the primary alcohols methanol, ethanol and 1-propanol, the decomposition rate induced by the TH effect decreased threefold as the number of carbon atoms increased from 1 to 3. No similar trend was observed for the MW effect. We deduce that the thermal effect is the major factor under microwave irradiation on increasing the carbon number.

3.3.2. Number of OH functions

Comparison of the dynamics of mineralization of ethanol versus ethylene glycol in Table 2 clearly shows an increase of both the MW effect and the TH–MW effect on increasing the number of OH functions. A similar increase of the TH–MW factor was also observed on comparing the dynamics for 1-propanol and glycerin; the increase in the MW effect in adding two more OH groups was somewhat subdued. Addition of an OH function to ethanol caused the rate of mineralization of ethylene glycol by the $\text{TiO}_2/\text{UV}/\text{MW}$ protocol to triple, whereas addition of two OH groups to 1-propanol led to a nearly sixfold increase in the rate of mineralization of glycerin. By contrast, only for the 1-propanol/glycerin case was the rate of mineralization of glycerin improved by the TH factor. Overall, an increase in the number of OH functions appears to lead to a more efficient transformation of a carbon to carbon

dioxide with the MW effect playing the major role, even though the mineralization process occurred at otherwise identical temperatures for both $\text{TiO}_2/\text{UV}/\text{CH}$ and $\text{TiO}_2/\text{UV}/\text{MW}$ protocols.

The dielectric loss factors of the model substrates reported in Table 1 show that, except for acetone and acetic acid, all the substrates have a dielectric loss factor greater than that of water used as the medium in all the mineralizations. Accordingly, microwave dielectric heating of these substrates was more efficient than for the surrounding aqueous medium. And although there were no temperature differences between the $\text{TiO}_2/\text{UV}/\text{CH}$ and $\text{TiO}_2/\text{UV}/\text{MW}$ methods, the process by which the substrates are energized by conventional heating or by microwave dielectric heating is dramatically different. Conventional heating energizes the aqueous medium first which then transfers the energy to the substrates, whereas dielectric heating energizes the substrates directly.

4. Concluding remarks

Dielectric loss factor data show that alcoholic substrates in an aqueous medium are heat-energized by priority absorption of the microwave radiation. As such, their oxidative degradation is promoted by directed localized dielectric heating. Thus the OH function may be an important key to examine and speculate on the microwave specific effect(s). By contrast, no trends were evident in the case of substrates bearing a carbonyl function, at least for the limited number of substrates examined in this study. Nonetheless, the mineralization of a substrate that bears a carboxyl function seems to be facilitated by the assistance of microwave radiation relative to a substrate that bears only a ketone function (e.g. compare the dynamics for acetic acid versus those for acetone). The microwave non-thermal effect was seen in all cases with MW factor ranging from 1.2 for 1-propanol to 4.1 for ethylene glycol.

References

- [1] Y. Ju, S. Yang, Y. Ding, C. Sun, A. Zhang, L. Wang, J. Phys. Chem. A 112 (2008) 11172–11177.
- [2] V. Církva, H. Žabová, Milan Hájek, J. Photochem. Photobiol. A: Chem. 198 (2008) 13–17.
- [3] S. Kataoka, D.T. Tompkins, W.A. Zeltner, M.A. Anderson, J. Photochem. Photobiol. A: Chem. 148 (2002) 323–330.
- [4] See e.g. M. Hájek, in: A. Loupy (Ed.), *Microwaves in Organic Synthesis*, 14, Wiley–VCH Verlag, Weinheim, Germany, 2002, pp. 345–378 (Chapter 14).
- [5] X. Zhang, D.O. Hayward, D.M.P. Mingos, Chem. Commun. (1999) 975–976.
- [6] S. Horikoshi, J. Tsuzuki, F. Sakai, M. Kajitani, N. Serpone, Chem. Commun. (2008) 4501–4503.
- [7] S. Horikoshi, F. Sakai, M. Kajitani, M. Abe, A.V. Emeline, N. Serpone, J. Phys. Chem. C, in press.
- [8] S. Horikoshi, F. Hojo, H. Hidaka, N. Serpone, Environ. Sci. Technol. 38 (2004) 2198–2208.
- [9] S. Horikoshi, A. Tokunaga, N. Watanabe, H. Hidaka, N. Serpone, J. Photochem. Photobiol. A: Chem. 177 (2006) 129–143.
- [10] S. Horikoshi, H. Hidaka, N. Serpone, Environ. Sci. Technol. 36 (2002) 1357–1366.
- [11] K. Hashimoto, T. Kawai, T. Sakata, J. Phys. Chem. 88 (1984) 4083–4088.
- [12] S. Horikoshi, F. Sakai, M. Kajitani, M. Abe, N. Serpone, Chem. Phys. Lett. 470 (2009) 304–307.